Graft Polymerization of Vinyl Acetate onto Starch. Saponification to Starch–*g*–Poly(vinyl Alcohol)

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Synopsis

Graft polymerizations of vinyl acetate onto granular corn starch were initiated by cobalt-60 irradiation of starch–monomer–water mixtures, and ungrafted poly(vinyl acetate) was separated from the graft copolymer by benzene extraction. Conversions of monomer to polymer were quantitative at a radiation dose of 1.0 Mrad. However, over half of the polymer was present as ungrafted poly(vinyl acetate) (grafting efficiency less than 50%), and the graft copolymer contained only 34% grafted synthetic polymer (34% add-on). Lower irradiation doses produced lower conversions of monomer to polymer and gave graft copolymers with lower % add-on. Addition of minor amounts of acrylamide, methyl acrylate, and methacrylic acid as comonomers produced only small increases in % add-on and grafting efficiency. However, grafting efficiency was increased to 70% when a monomer mixture containing about 10% methyl methacrylate was used. Grafting efficiency could be increased to over 90% if the graft polymerization of vinyl acetate–methyl methacrylate was carried out near 0°C, although conversion of monomers to polymer was low and grafted polymer contained 40–50% poly(methyl methacrylate). Selected graft copolymers were treated with methanolic sodium hydroxide to convert starch–*g*–poly(vinyl acetate) to starch–*g*–poly(vinyl alcohol). The molecular weight of the poly(vinyl alcohol) moiety was about 30,000. The solubility of starch–*g*–poly(vinyl alcohol) in hot water was less than 50%; however, solubility could be increased by substituting either acid-modified or hypochlorite-oxidized starch for unmodified starch in the graft polymerization reaction. Vinyl acetate was also graft polymerized onto acid-modified starch which had been dispersed and partially solubilized by heating in water. A total irradiation dose of either 1.0 or 0.5 Mrad gave starch–*g*–poly(vinyl acetate) with about 35% add-on, and a grafting efficiency of about 40% was obtained. A film cast from a starch–*g*–poly(vinyl alcohol) copolymer in which homopolymer was not removed exhibited a higher ultimate tensile strength than a comparable physical mixture of starch and poly(vinyl alcohol).

INTRODUCTION

The use of renewable, agriculturally derived products such as polysaccharides as extenders and replacements for synthetic, petroleum-based polymers is currently an active area for research. Graft polymerization of vinyl and acrylic monomers onto a polysaccharide backbone offers perhaps one of the best ways to utilize polysaccharides for this purpose. The Northern Regional Research Center has extensively studied graft polymerizations onto starch; as one phase of this continuing program, we have investigated the cobalt 60-initiated free-radical graft polymerization of vinyl acetate and the subsequent hydrolysis of the resulting graft copolymers to starch–*g*–poly(vinyl alcohol).

The literature contains only a few reports of starch–vinyl acetate graft polymerizations. Walrath, Reyes, and Russell[1] found that cobalt-60 irradiation of mixtures of wheat starch and vinyl acetate in the absence of solvent gave largely ungrafted homopolymer. In the presence of methanol:water (3:2 by volume),

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graft copolymers contained about 15% grafted poly(vinyl acetate), and grafting efficiency [percentage of the total poly(vinyl acetate) formed which was grafted to starch] was about 40%.[2] Reaction of preirradiated starch with vinyl acetate, either in a water emulsion or without diluent, gave only low conversions to grafted poly(vinyl acetate).[1,2] Brockway[3] graft polymerized vinyl acetate onto starch with a hydrogen peroxide–ferrous ammonium sulfate–ascorbic acid initiating system and reported that grafting efficiency could be increased by including minor amounts of certain comonomers, particularly methyl methacrylate and methacrylic acid, with the vinyl acetate.

EXPERIMENTAL

Materials

Pearl corn starch (Globe 3005) containing about 12% water was from CPC International. Acid-modified corn starch was Clinton 290B (water content about 12%) from Clinton Corn Processing Company. Hypochlorite-oxidized starch was Superfilm 40 (water content about 15%) from Stein, Hall and Company, Inc.

Vinyl acetate (Polysciences), methyl acrylate (Eastman), and methyl methacrylate (Eastman) were distilled at atmospheric pressure through a 22-in. Vigreux column; and methacrylic acid (Polysciences) was distilled onto a cold-finger condenser at 0.5 mm before use. Acrylamide (Eastman) was used as received.

Graft Polymerizations

The cobalt-60 source was a Gammacell 200 unit from Atomic Energy of Canada, Ltd. Dose rate at the center of the chamber was 0.87–0.67 Mrad/hr, as calculated from the initial dosimetry data provided by the manufacturer and the decay rate of cobalt 60. This variation was the result of decay during the research period.

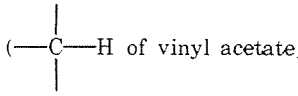
For graft polymerizations onto granular starch, a wide-mouth, screw-cap bottle was charged with starch, vinyl acetate, comonomer (when used), and water (1 ml for 4 g, dry basis, of starch). The mixture was blended thoroughly with a spatula, and the paste-like mass was evacuated to 100 mm and repressured with nitrogen four times to remove dissolved oxygen. About 5–10% of the volatile monomer was lost by this evacuation procedure. The bottle was capped, irradiated with cobalt 60 to the required total dose, and allowed to stand at ambient temperature for 2 hr. The reaction mass was extracted several times with benzene by prolonged stirring at room temperature, and the extracted graft copolymer and benzene-soluble homopolymer were both isolated by freeze drying. The weight percent synthetic polymer in the graft copolymer (% add-on) was determined by weight gain of starch due to graft polymerization.

For graft polymerizations onto stirred, acid-modified starch dispersions, a 4-oz screw-cap bottle was charged with either 8.0 or 10.0 g (dry basis) acid-modified starch and 70 ml water containing 0.05 g dodecylbenzene sodium sulfonate. The mixture was heated on a steam bath to 90°C and cooled to 25°C, and 10.0 g vinyl acetate was added. The dispersion was shaken vigorously and a mechanical stirrer was inserted through the screw cap, which contained a hole just large

enough to accommodate the stirrer shaft. The reaction mass was placed in the cobalt-60 source and irradiated with continuous stirring to the required dose. After irradiation, the mixture was allowed to stand for 2 hr at ambient temperature and was then freeze dried. The dry solid was moistened to a water content of about 30% and extracted several times with benzene by prolonged stirring at room temperature. Polymer fractions were isolated by freeze drying, and % add-on was calculated from the weight gain of starch.

Methyl Methacrylate Content of Poly(vinyl Acetate–*co*–methyl Methacrylate)

Percentages of methyl methacrylate in both grafted and ungrafted synthetic polymers were calculated from the 100-MHz NMR spectra as determined in benzene-D_6 (5% solutions). Spectra were run on a Varian HA-100 spectrometer. Signals at δ 5.16



and δ 3.36 ($-OCH_3$ of methyl methacrylate) were integrated, and the mole-% methyl methacrylate was calculated from the following equation:

$$\text{mole-\% methyl methacrylate} = \frac{\text{integrated } \delta \text{ 3.36 signal} \div 3}{(\text{integrated } \delta \text{ 3.36 signal} \div 3) + (\text{integrated } \delta \text{ 5.16 signal})} \times 100$$

Weight-% methyl methacrylate was then readily calculated. The method was checked with known synthetic mixtures of poly(methyl methacrylate) and poly(vinyl acetate) and gave good agreement with theory (Table I).

For analysis of grafted synthetic polymer, it was first necessary to remove the starch moiety to obtain a benzene-soluble polymer. The perchloric acid hydrolysis method of Dennenberg and Abbott[4] gave quantitative removal of starch. To confirm that this method was not altering the composition of grafted polymer, a sample of poly(vinyl acetate–*co*–methyl methacrylate) containing 4.5 wt-% methyl methacrylate (by NMR) was subjected to the conditions of starch hydrolysis. The methyl methacrylate content of the polymer was unchanged.

Hydrolysis of Starch–*g*–Poly(vinyl Acetate) to Starch–*g*–Poly(vinyl Alcohol)

A dispersion of 10 g starch–*g*–poly(vinyl acetate) in 125 ml absolute methanol containing 1.25 ml 40% sodium hydroxide solution was heated under reflux for

TABLE I
Weight-% Poly(methyl Methacrylate) in Physical Mixtures with Poly(vinyl Acetate)

Calculated	Found by NMR
4.8	4.4
10.8	11.2
20.0	22.3

30 min. The solid was separated by filtration, transferred to a Soxhlet extractor, and extracted overnight with methanol. The extracted solid was allowed to air dry at room temperature. Infrared analysis of the product showed no acetate carbonyl.

Water Solubility of Starch-*g*-Poly(vinyl Alcohol)

To determine solubility at 100°C, a stirred suspension of 0.5 g starch–*g*–poly(vinyl alcohol) in 375 ml water was heated in a boiling water bath for 30 min. The dispersion was cooled to room temperature and a portion was centrifuged for 20 min at 4900 × *g*. Percent solubility was calculated from the weights of solid obtained by freeze drying 50-ml portions of both the uncentrifuged dispersion and the supernatant.

Solubility at room temperature was determined by allowing a dispersion of 5.00 g graft copolymer in 100 ml water to stir overnight. The dispersion was centrifuged and the percent solubility was calculated from the weight of freeze-dried solid obtained from a known weight of supernatant.

Removal of Starch from Starch–*g*–Poly(vinyl Alcohol) and Determination of Graft Molecular Weight

A dispersion of 5.00 g starch–*g*–poly(vinyl alcohol) in 200 ml water was heated on a steam bath for 15 min at 90–95°C and then cooled to about 60°C. The pH was adjusted to 4.4 with dilute hydrochloric acid and 1 ml Diazyme L100 enzyme solution (Miles Laboratories, Inc.) was added to hydrolyze the starch component to low molecular weight sugars. The mixture was held at 60°C overnight, the enzyme was destroyed by heating to about 95°C, and the mixture was dialyzed against distilled water for two to three days with frequent changes of water. The dialyzed solution was centrifuged to remove about 0.2 g insolubles, and the soluble poly(vinyl alcohol), containing less than 5% carbohydrate by infrared, was isolated by freeze drying. A % add-on value was calculated from the loss in weight of the graft copolymer on enzyme hydrolysis.

Number-average molecular weights were determined in either 0.15*N* or 0.5*N* sodium chloride solution on a Melabs Model CSM-2 membrane osmometer equipped with a B-19 membrane (Schleicher and Schuell Co.). The higher sodium chloride normality was used for the grafted poly(vinyl alcohol) obtained with dispersed, acid-modified starch, since these samples did not give straight line plots of π/c versus c in 0.15*N* sodium chloride.

Preparation and Testing of Films

A dispersion of 7.0 g (dry basis) starch–*g*–poly(vinyl alcohol) which still contained homopolymer, 35 ml water, and 1.75 g glycerol was prepared in a 250-ml round-bottomed flask containing two glass marbles to facilitate stirring. The flask was rotated in a boiling water bath for 30 min according to the method of Otey et al.,[5] and the resulting hot dispersion was then centrifuged for 2 min at about 200 × *g* to remove a few residual air bubbles. The dispersion was finally cast at 0.015-in. wet thickness onto a glass plate and dried for 5 min in a forced-air oven at 100°C. The resulting transluscent film (0.0016–0.0018 in. thick) was cut into 0.590-in. strips and allowed to stand for two days at 22°C and 50% relative humidity.

Films from poly(vinyl alcohol)–starch physical mixtures were prepared from 6.8 g (dry basis) acid-modified corn starch, 3.2 g poly(vinyl alcohol) (Vinol 205, Air Products and Chemicals, Inc.), and 2.5 g glycerol in 40 ml water. This higher solids concentration was necessary to obtain a dispersion viscosity suitable for film casting. The thickness of dry films was 0.0017–0.0019 in.

Ultimate tensile strengths of film strips were obtained on an Instron Universal Testing Instrument with a grip separation of 10 cm and a cross-head speed of 5 cm/min. Four separate films were cast for each determination, and each film was cut into seven strips for tensile strength measurement. Ultimate tensile strengths of the four sets of films agreed to within ±10%.

RESULTS AND DISCUSSION

Graft polymerizations of vinyl acetate onto granular corn starch were initiated by the cobalt-60 irradiation of mixtures of starch (4 g), water (1 ml), and varying amounts of monomer. The procedure was similar to that reported by us earlier[6] for the graft polymerization of styrene; and as observed with styrene, mixtures were converted to semisolid pastes by thorough blending. Mixtures were prepared in screw-cap bottles, and oxygen was displaced by evacuation followed by repressuring with nitrogen. About 10% of the volatile monomer was typically lost during oxygen displacement. After graft polymerization, each reaction product was extracted with benzene to remove ungrafted poly(vinyl acetate), and a % add-on was calculated from the gain in weight of starch due to graft polymerization. The percentage of the total polymer formed which was unextractable with benzene was then calculated as the grafting efficiency.

As expected, the amount of monomer and the total radiation dose used to initiate polymerization influenced the total conversion and efficiency of the grafting reaction (Table II). Total conversions of vinyl acetate to polymer were quantitative at 1 Mrad. Lower radiation doses produced lower conversions to polymer; and at 0.1 Mrad, total conversion was only 15%. Values for % add-on also decreased with decreasing radiation dose and showed a maximum value of 34% at 1 Mrad. Grafting efficiencies did not vary greatly with radiation dose and were in the range of 38–47% for the three reactions. A higher grafting efficiency (68%) was obtained when about half the amount of starting monomer was

TABLE II
Graft Polymerizations onto Granular Starch. Influence of Irradiation Dose and Amount of Vinyl Acetate[a]

VAC,[b] g	Dose, Mrad	% Add-on[c]	Conversion, %		Grafting efficiency,[d] %
			To graft	To homopolymer	
4.6	1.0	34	44	56	44
4.5	0.5	25	29	48	38
4.4	0.1	7	7	8	47
2.3	1.0	30	68	32	68

[a] Granular unmodified corn starch (4.0 g) and 1 ml water were used. Dose rate was 0.87 Mrad/hr.

[b] Vinyl acetate, started with 5 g in the first three reactions and 3 g in the last reaction. Losses are due to evacuation to remove dissolved oxygen.

[c] Determined from weight gain of starch after benzene extraction.

[d] Grafting efficiency = $\frac{\text{conversion of monomer to grafted polymer}}{\text{total conversion of monomer to polymer}}$.

used; however, because of the reduced amount of monomer, the add-on was only 30%. Graft polymerizations were allowed to proceed at ambient temperature with no external cooling. Under the conditions of the first reaction of Table II, a maximum temperature of 58°C was reached during cobalt-60 irradiation.

Since Brockway[3] increased grafting efficiency by including minor amounts of selected comonomers, particularly methyl methacrylate and methacrylic acid, in his polymerization mixture, we investigated the addition of acrylamide, methyl acrylate, methacrylic acid, and methyl methacrylate comonomers to our graft polymerization system (Table III). Reactions in Table III were initiated with a total dose of 0.5 Mrad, so results should be compared with the second reaction of Table II. Except for the fourth reaction of Table III, which used a partially neutralized methacrylic acid, values for % add-on and grafting efficiency were higher when comonomers were added. Although most of these increases were small, the addition of methyl methacrylate increased grafting efficiency to 70%, largely through decreased conversion to homopolymer. For this reason, we examined more thoroughly the graft polymerization of vinyl acetate in the presence of methyl methacrylate comonomer.

In our study of the vinyl acetate–methyl methacrylate system, we varied the amount of methyl methacrylate used, the total radiation dose, and the reaction temperature (Table IV). We then determined the effects of these variations on % add-on, total conversion to polymer, grafting efficiency, and the amount of methyl methacrylate incorporated in both grafted polymers and homopolymers. Relative amounts of the two repeating units were determined by NMR.

For the graft polymerizations at 0°C, starch–monomer–water mixtures were first cooled in ice water for 30 min and then irradiated with cobalt 60 in ice-filled containers. After irradiation, mixtures were kept in ice water for 2 hr before products were isolated. Graft polymerizations carried out in ice water rather than at ambient temperatures gave lower values for % add-on as well as lower conversions of monomer to polymer (second versus first reaction and third versus fifth reaction of Table IV). Total conversion of monomers to polymer was about 15% at 0.5 Mrad and 0°C, and this value was increased to only 32% when 2 Mrad was used. Although grafting efficiencies were higher at lower temperatures, high percentages of poly(methyl methacrylate) were found in grafted synthetic polymers. For example, when polymerization was carried out in ice water at 0.5 Mrad, the grafted polymer consisted of about half poly(methyl methacrylate),

TABLE III
Graft Polymerizations onto Granular Starch. Influence of Comonomers[a]

Comonomer, g	% Add-on	Conversion, %		Grafting efficiency, %
		To graft	To homopolymer	
Acrylamide, 0.4	32	40	41	49
Methyl acrylate, 0.5	32	37	36	51
Methacrylic acid, 0.5	29	32	34	48
Methacrylic acid, 0.5, (pH 4.4)[b]	21	21	41	34
Methyl methacrylate, 0.5	28	30	13	70

[a] Granular unmodified starch (4.0 g), 1 ml water, and 5.0 g vinyl acetate were used. Loss of volatile monomers due to evacuation to remove dissolved oxygen amounted to 0.2–0.4 g. Dose rate was 0.74–0.71 Mrad/hr, and total dose was 0.5 Mrad.

[b] Methacrylic acid (0.5 g) was partially neutralized with sodium hydroxide.

TABLE IV
Influence of Reaction Variables on Graft Polymerization onto Granular Starch in the Presence of Methyl Methacrylate[a]

Reaction number	Methyl methacrylate, g	Dose, Mrad	Temperature	% Add-on	Conversion, %		Grafting efficiency, %	Wt-% poly(methyl methacrylate)	
					To graft	To homopolymer		In graft	In homopolymer
1	0.5	0.5	ambient	28	30	13	70		
2	0.5	0.5	0°C	16	14	0.7	95	49	
3	0.5	1.0	0°C	22	22	2	92	38	54
4	0.5	2.0	0°C	26	28	4	88	39	25
5	0.5	1.0	ambient	44	60	40	60	16	4.5
6	0.5	1.0	varied[b]	29	31	12	72		
7	0.5	1.0	varied[c]	26	26	4	87		
8	1.0[d]	1.0	ambient	50	73	27	73	26	11

[a] Granular unmodified starch (4.0 g), 1.0 ml water, and 5.0 g (except for last reaction) vinyl acetate were used. Loss of volatile monomers due to evacuation to remove dissolved oxygen amounted to 0.2–0.4 g. Dose rate was 0.71–0.70 Mrad/hr.

[b] Cooled to 0°C and then irradiated at ambient temperature.

[c] Irradiated to 0.5 Mrad at 0°C and then irradiated to 0.5 Mrad at ambient temperature.

[d] Started with 4.5 g vinyl acetate.

even though methyl methacrylate represented only about 10% of the total starting monomer mixture. At ambient temperature and with methyl methacrylate:vinyl acetate monomer ratios approximating either 10:90 or 20:80, the methyl methacrylate content of the grafted polymer was only slightly higher than that of the initial monomer mixture (fifth and eighth reaction of Table IV).

To investigate the effect of intermediate temperatures, a starch–monomer–water mixture was first cooled in ice water for 30 min and then irradiated to 1 Mrad and allowed to polymerize at ambient temperature (sixth reaction, Table IV). In the seventh reaction, the first 0.5 Mrad of irradiaton was performed in ice water while the rest of the irradiation and reaction was allowed to take place with no external cooling. These two reactions gave values for % add-on, % conversion, and grafting efficiency that were between those obtained at ambient and ice water temperatures.

Selected graft polymerizations were next repeated on a larger scale with both unmodified and modified starches to provide sufficient graft copolymer for alkaline saponification to starch–*g*–poly(vinyl alcohol) (Table V). Reactions were carried out with no external cooling, and the first reaction of Table V (a fivefold scale-up of the fifth reaction of Table IV) reached a maximum temperature of 67°C during cobalt-60 irradiation. The other three reactions of Table V were fivefold scale-ups of the first reaction of Table II and used unmodified, acid-modified, and hypochlorite-oxidized corn starches. Values for % add-on and grafting efficiency in Table V were lower than for comparable smaller scale reactions, particularly when the modified starches were used.

Hydrolyses of starch–*g*–poly(vinyl acetate) to starch–*g*–poly(vinyl alcohol) were carried out in refluxing methanolic sodium hydroxide; and the absence of acetate carbonyl absorption in infrared spectra indicated that hydrolyses were complete. The starch moiety was then removed from a portion of starch–*g*–poly(vinyl alcohol) by enzymatic hydrolysis, and the molecular weight of the remaining poly(vinyl alcohol) was determined by membrane osmometry. The % add-on of poly(vinyl alcohol), as determined by weight loss of a graft copolymer on enzymatic hydrolysis, was less than the % add-on of the corresponding poly(vinyl acetate) graft copolymer because of the loss in molecular weight of the vinyl acetate repeating unit on alkaline hydrolysis to the alcohol.

The molecular weight of 30,000 for poly(vinyl alcohol) could represent a lower degree of polymerization than that of the poly(vinyl acetate) precursor because of the possibility of branching in poly(vinyl acetate) and the subsequent hydrolytic cleavage of these branches by methanolic sodium hydroxide.[7] We have not investigated the question of branching in grafted poly(vinyl acetate) and have not determined whether ungrafted poly(vinyl alcohol) fragments are present in starch–*g*–poly(vinyl alcohol) due to debranching. Although the starch–*g*–poly(vinyl alcohol) products from the first two reactions of Table V were slightly soluble in water at room temperature, these soluble fractions cannot totally represent cleaved poly(vinyl alcohol) branches, since infrared spectra of soluble fractions also show the presence of considerable carbohydrate.

Since the amylose and amylopectin components of starch have number-average molecular weights on the order of 10^5 and 10^6, respectively,[8,9] a grafting frequency of about 10^3 anhydroglucose units per graft would correspond to an average of 1 poly(vinyl alcohol) graft per amylose molecule and 10 grafts per amylopectin molecule, assuming no degradation of the polysaccharide on irradiation. It has been shown by Hofreiter,[10] however, that the molecular weight of starch is re-

TABLE V
Graft Polymerizations of Vinyl Acetate and Hydrolysis to Starch–*g*–Poly(vinyl Alcohol)[a]

	Graft polymerization			Starch–*g*–poly(vinyl alcohol)				
							Solubility, %	
Starch	Methyl methacrylate, g	% Add-on[b]	Grafting efficiency, %	% Add-on[c]	$\overline{M}_n$ of graft[d]	AGU/graft[e]	Room temp.	100°C
Unmodified corn	2.5	38[f]	55	25	—[g]		4	26
Unmodified corn	0	30	35	14	30,000	1100	5	45
Acid modified corn	0	21	23	10	30,000	1700		77
Hypochlorite-oxidized corn	0	15	15	8				94

[a] Starch (20 g), 5 ml water, and 25 g vinyl acetate were used. Total dose was 1.0 Mrad (dose rate: 0.71–0.67 Mrad/hr). There was about a 10% loss of volatile monomers due to evacuation to remove dissolved oxygen.

[b] Determined from weight gain of starch.

[c] Determined from weight loss of graft copolymer on enzyme hydrolysis.

[d] Determined by membrane osmometry in 0.15*N* sodium chloride solution.

[e] Grafting frequency: average number of anhydroglucose units per graft.

[f] Grafted polymer contains 18% poly(methyl methacrylate).

[g] Not determined. About half of the grafted polymer was water insoluble.

TABLE VI
Graft Polymerizations onto Stirred Acid-Modified Starch Dispersions. Influence of Radiation Dose[a]

	Starch–*g*–poly(vinyl acetate)				Starch–*g*–poly(vinyl alcohol)	
Dose, Mrad	% Add-on[b]	Conversion to graft, %	Conversion to homopolymer, %	Grafting efficiency, %	% Add-on[c]	Solubility, % at 100°C
1.0	35	43	57	43	21[d]	86
0.5	33	40	58	41	22[d]	
0.1	8	7	13	35	5	

[a] Reaction mixtures contained 8.0 g acid-modified corn starch, 10.0 g vinyl acetate, 70 ml water, and 50 mg dodecylbenzene sodium sulfonate. Dose rate was 0.67 Mrad/hr.

[b] Determined from weight gain of starch.

[c] Determined from weight loss of graft copolymer on enzyme hydrolysis.

[d] $\overline{M}_n$ of grafted poly(vinyl alcohol) is about 60,000, as determined by membrane osmometry in 0.5*N* NaCl solution. Grafting frequency is about 1400 AGU/graft.

duced by gamma irradiation, so the average number of grafts per starch molecule would be less in actual practice.

Since solubility of starch–*g*–poly(vinyl alcohol) would be an important factor in any end-use application, solubilities in water at 100°C are given in Table V for the graft copolymers. Although the graft copolymer prepared from unmodified starch in the absence of methyl methacrylate would swell and disperse in hot water, less than half of the polymer actually dissolved. This was not surprising, since we have also observed low water solubilities with other hydrophilic starch graft copolymers.[11,12] As expected, solubility greatly improved when acid-modified or hypochlorite-oxidized starches were substituted for unmodified starch in the graft polymerization reaction. Use of methyl methacrylate as a comonomer reduced water solubility of the poly(vinyl alcohol)-containing graft copolymer to 26% and gave grafted synthetic polymer that was only partially soluble in water after removal of starch by enzymatic hydrolysis.

Since our studies up to this point involved graft polymerizations onto granular starch, we wondered how the graft polymerization of vinyl acetate might proceed if starch were dispersed and partially dissolved in hot water before polymerization. Three graft polymerizations were therefore run with stirred water dispersions of acid-modified corn starch using different total doses of cobalt-60 irradiation to initiate polymerization (Table VI). Acid-modified starch was used so that a high percentage of the starch would be water soluble and also so that starch dispersions would be thin enough to allow stirring during irradiation. Vinyl acetate was emulsified by the addition of dodecylbenzene sodium sulfonate to the aqueous system.

Comparison of results in Table VI with those shown in Table II for unmodified granular starch shows about the same % add-on and grafting efficiency when a total dose of 1.0 Mrad is used. However, at 0.5 Mrad, both the % add-on and the total conversion of vinyl acetate to polymer were higher when the graft polymerization was carried out with partially dissolved, acid-modified starch. With a total dose of 0.1 Mrad, both sets of reaction conditions gave low values for both % add-on and total conversion to polymer.

The starch–*g*–poly(vinyl acetate) products of Table VI were hydrolyzed to starch–*g*–poly(vinyl alcohol) as in Table V. As expected, grafting onto acid-modified starch gave starch–*g*–poly(vinyl alcohol) that was largely soluble in hot water. The molecular weight of grafted poly(vinyl alcohol) was about 60,000.

We briefly examined the preparation and properties of films cast from water dispersions of starch–*g*–poly(vinyl alcohol). To provide sufficient material for testing, a number of replicate graft polymerizations were run under the same conditions as the second reaction of Table VI, except that 10 g acid-modified corn starch was used to provide a reaction mixture containing equal weights of starch and monomer. Reaction products were then combined. Since ungrafted poly(vinyl acetate) would not be extracted from the graft copolymer in any practical process, homopolymer was not removed, and the entire reaction product was hydrolyzed in methanolic sodium hydroxide. The hydrolyzed product contained 33% (by weight) poly(vinyl alcohol). Films containing 20% (by weight) glycerol plasticizer had ultimate tensile strengths on the order of 1200 psi, as compared with 800 psi for films cast from a synthetic mixture containing the same proportions of acid-modified starch and commercial poly(vinyl alcohol).

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trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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